Coupling of reactive polystyrene and polyethylene in melts

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Polystyrene (OPS) having oxazoline groups and polyethylene (CPE) having carboxyl groups were melt blended in a Rheomix mixer. The effects of composition on the torque, thermal transitions, solubility and phase structure of these resulting polymer alloys were investigated. Differential scanning calorimetry (d.s.c.) and scanning electron microscopy (SEM) data on these alloys is compared with the corresponding melt blends of the non-reactive polymers. The torque–time relationship, phase structure and thermal properties of these polymer alloys were found to be very different from the non-reactive blends, and this was more so in an alloy with 40% CPE. This is attributed to the coupling reaction between the OPS and CPE. Studies on extraction of this alloy in xylene support the presence of a crosslinked polymer. The Fourier transform infra-red (*FT*i.r.) spectra of alloys and their low molecular weight analogues show that amido–ester linkages similar to the model compounds are formed between OPS and CPE.

(Keywords: coupling; oxazoline; polymer alloys; polymer blends; graft polymer; amido–ester)

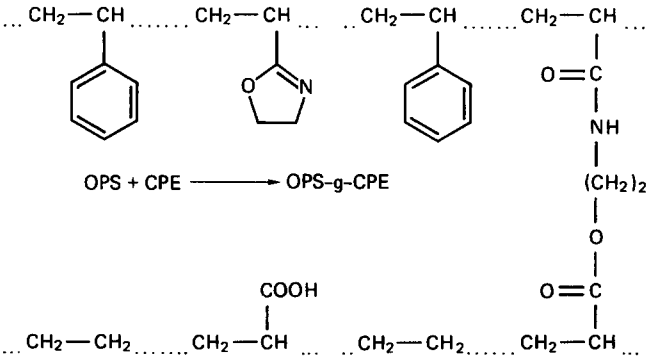
INTRODUCTION

There are economic advantages to producing improved polymer materials by modifying existing polymers rather than producing new polymers. Polymers such as polystyrene (PS) and polyethylene (PE) have useful properties of their own; but when blended together the resultant blend is incompatible and its physical properties are generally poor. So, it is desirable to produce PE–PS compatible blends in a cost effective way. Earlier methods of achieving this consisted of adding well defined block and graft copolymers PS-b-PE and PS-g-PE to PS and PE blends[1]. Improvements in mechanical properties were also obtained when PS and PE were chemically bonded using peroxide, and then this reacted polymer was incorporated as a solid phase dispersant, in PS–PE blends[2]. The emulsification effect of poly(hydrogenated butadiene-g-styrene) polymer also resulted in PS–PE blends with a much improved balance of properties, over a broad composition range[3–5]. This effect was attributed to the preferential location of the block copolymer at the interface between PS and PE phases.

Block polymers, crosslinking, or interpenetrating networks techniques are being used for controlling morphology and mechanical properties of the incompatible polymer blends, but these methods are not necessarily the preferred ones. Recently more attention has been focused on reactive polymer processing, in which superior polymer alloys are produced during melt processing, making it an attractive cost effective alternative. Some recent review articles have highlighted the significance of reactive polymer processing[6–8]. In this case polymers are reacted through their functional groups while being processed, and the processing equipment such as an extruder or mixer acts as a mini reactor.

It has been known for many years that oxazoline homopolymers and copolymers can be crosslinked with a wide variety of reagents, including carboxylic acids[9], resulting in amido–ester crosslinking units[10,11]. Despite this, interpolymer reactions through this type of functional group were hardly reported until recently[6], and the art remained confined primarily to the patent literature. It has been claimed that, when melt blended, reactive polystyrene (OPS) and polyethylene (CPE), with oxazoline and carboxylic acid functionality, respectively, produce an alloy with better impact strength and tensile properties than the ordinary PE–PS blends. The improvement in properties is attributed to the type of crosslinking between the two polymers shown in Scheme 1.

It is understood that crosslinking, hydrogen bonding and other polar interactions in polymer blends enhance their compatibility and improve their mechanical properties; so, the same effect can be expected from the coupling reaction which results in amido–ester linkages. However, very little is known about the chemistry and kinetics of this reaction, and since it is a melt reaction it is further complicated in this respect. In this work thermal and morphological properties, and the chemical structure of this polymer alloy have been studied. We expect this will lead to a better understanding of structure–property relationships of this type of polymeric alloy.



Scheme 1

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EXPERIMENTAL

Materials

All the polymers used in this work were supplied by Dow Chemical Company. They were in pellet form and were used without further purification or treatment. Reactive polyethylene (CPE), Primacor 1430, was reported to have 9 mol% functional carboxylic acid, and reactive polystyrene (OPS), XUS-140056.01, was reported to have 1 mol% oxazoline functionality. Low density polyethylene (PE), polyethylene 746, and polystyrene (PS), Styron 685, were commercial grade polymers. A high molecular weight hindered phenol antioxidant (AO), Irganox 1010, was used in all the melt blends.

2.Ethyl hexanoic acid and 2.ethyl oxazoline were obtained from Aldrich Chemical Co. and were used in the preparation of model compounds.

Procedures

To achieve efficient mixing under well controlled conditions, the two polymers were melt blended in a Haake–Buchler Reomix mixer Model 600, with roller blades. Microcomputer provisions on this equipment permitted control of the mixing variables. A 40 g charge of OPS and CPE in desired proportions was dry blended and then fed into the mixer, which already had been adjusted to required conditions. After two minutes of initial mixing 0.1 wt% antioxidant was added to the polymer melt, and the mixing was continued for the set time. Torque and temperature were displayed on the screen as a function of time. All the alloys were mixed at 225°C, for 30 min and at 100 r.p.m.

For the purpose of comparative study, corresponding blends of non-reactive polymers (PE–PS) with similar viscosity characteristics were prepared under the same conditions. Dry blends of reactive polymers were also prepared by first grinding the polymers to powder and then mixing them in desired proportions, and finally this mixture was homogenized in a blender at room temperature.

Polymer alloys prepared and used in this work are listed in *Table 1*.

Films of various thicknesses (50–250 μm) of these blends were pressed out at 170°C for 4 min and were subsequently used in characterization work.

Characterization

CPE is insoluble in common organic solvents at room temperature, whereas OPS is readily soluble in toluene at this temperature. CPE, on the other hand, is soluble in xylene at about 100°C. Solubility of the alloys, after being finely subdivided, was tested in toluene; and one of these OPS–CPE alloys with 40% CPE was subjected to Soxhlet extraction in toluene and xylene for different lengths of time. After re-precipitation and washing in methanol both the soluble and insoluble fractions were dried and further characterized.

Fourier transform infra-red (*FT*i.r.) spectroscopy was performed on a Bruker IFS-85 spectrophotometer. Films 50 μm thick were used and the spectrum was obtained in the region 4000–400 cm^{-1}.

Thermograms of individual polymers, their alloys, dry and melt blends, and that of toluene- and xylene-extracted samples were obtained on a Perkin–Elmer differential scanning calorimeter Model DSC-2C. The instrument was attached to a microcomputer so that results for melting point (T_m) and heat of fusion (ΔH) could be easily analysed. Indium was used for the calibration of the instrument and then circular discs which had been cut from polymer films, weighing 2–5 mg, were encapsulated in aluminium pans. The thermograms were obtained at a heating rate of 20 K min^{-1} in the region 300–500 K.

Scanning electron micrographs of polymer blends were taken on a JEOL Model JSM 84 microscope. Samples were prepared by fracturing the blend under liquid nitrogen to obtain a surface area of 2–3 mm^2. These samples were then gold coated on Edwards high vacuum equipment. Representative micrographs were taken in the magnification range 2000–50 000.

2.Ethyl hexanoic acid and 2.ethyl oxazoline were chosen as low molecular weight chemical analogues for CPE and OPS, respectively. These two reagents were reacted *in situ* under nitrogen atmosphere for 24 h at 80°C. The resulting compound was analysed by *FT*i.r. spectroscopy and its spectrum was compared with the OPS–CPE alloy.

Table 1 OPS–CPE alloys mixed at 225°C, for 30 min at 100 r.p.m.

Sample no.	Composition (CPE wt%)
1	10
2	20
3	30
4	40
5	50
7	70

Extraction of sample 4 in toluene and xylene

4E	Insoluble fraction in toluene after 24 h
4S	Soluble fraction in toluene after 24 h (~1%)
4EX	Insoluble fraction in xylene after 24 h
4SX	Soluble fraction in xylene after 24 h (~5%)
4EXW	Insoluble fraction in xylene after one week
4SXW	Soluble fraction in xylene after one week (~35%)

RESULTS AND DISCUSSION

Reactive polymer blends, i.e. alloys, can be fairly easily tested for their mechanical properties, but the chemical characterization of such systems always poses practical problems. These include the difficulties of finding a suitable solvent, detection of very low concentrations of new chemical groups being formed during the melt processing, and the complications arising due to degradation of some polymers at high temperature. In OPS–CPE system, OPS contains only 1 mol% oxazoline and, even if one ignores the rheological constraints on the extent of reaction, one can hardly expect that the concentration of the amido–ester linkages will exceed 0.5 mol%. Taking into account all these difficulties we used a number of techniques to obtain the evidence for the coupling reaction between the functional groups of OPS and CPE.

Melt reaction between these two polymers will result in an increase in molecular weight and viscosity, and this in turn is expected to be manifested by an increase in torque during the mixing. The torque–time relationship for OPS–CPE (90/10) blend is shown in *Figure 1*, and is compared with the corresponding unreactive blend (PS–PE) and a blend with only one component reactive

(PS–CPE). After an initial melting and mixing period a slight increase in torque can be noticed for the reactive blend, whereas in the other two cases, where no reaction is expected, a slow decline in torque is observed. Although in this composition the reactive groups in OPS and CPE are equimolar, an increase in torque does not indicate that intermolecular reaction has taken place to any significant extent. Plots of blends with higher CPE content are shown in *Figure 2*. There is a substantial increase in torque for 40% CPE composition, but with a further increase in CPE content this increase in torque diminishes again. If increase in torque is accepted to be an indicator of polymer reactivity, then under the experimental conditions it can be safely assumed that maximum reaction occurs in blends with about 40% CPE.

The solubility characteristics of these polymer alloys in toluene also coincide with the above findings. The 10% CPE alloy was found, surprisingly, to be soluble in toluene at room temperature, although toluene is a non-solvent for CPE itself. With further increase of CPE content to 20 and 30% the alloys become partially soluble in toluene, and they are almost insoluble in toluene when

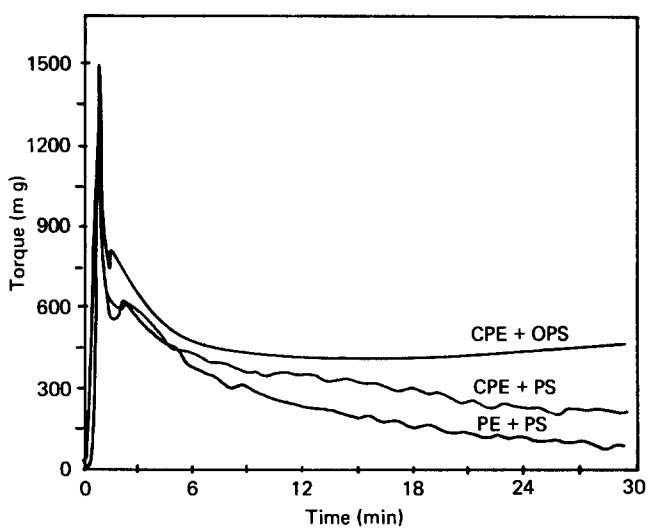

Figure 1 Torque–time relationship for various polystyrene–polyethylene blends, with 10% polyethylene

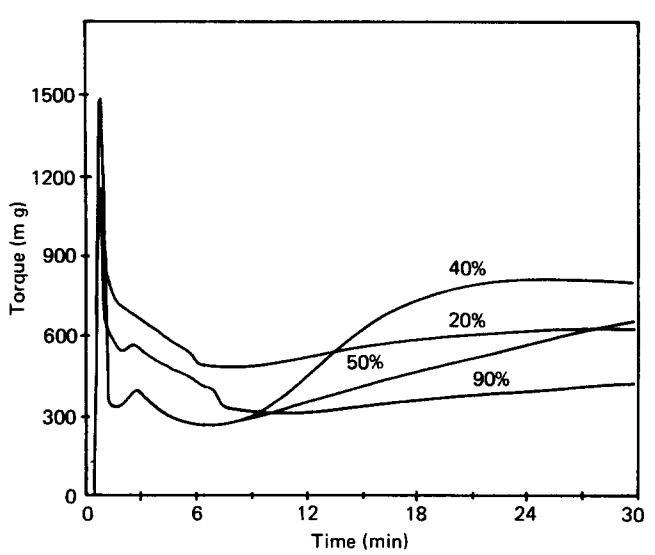

Figure 2 Torque–time relationship for OPS–CPE alloys. Numbers on the curves indicate CPE content (wt%) in the alloy

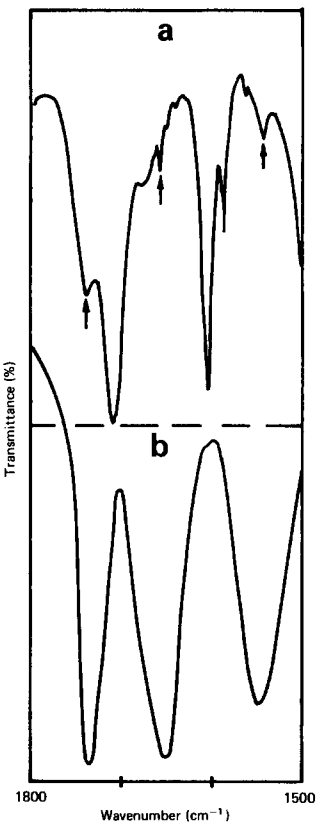

Figure 3 *FTi.r.* spectra of: (a) the insoluble fraction of OPS–CPE (60/40) alloy after one week. Arrows indicate peaks matching the model compounds. (b) Model compounds obtained by reacting 2.ethyl hexanoic acid and 2.ethyl oxazoline

CPE content is 40%. On the other hand, when the solubility of unreactive blends (PS–PE) of the same composition were tested in toluene, the PE fraction remained undissolved, while the PS dissolved. This again suggests that the melt mixing of OPS and CPE in 60:40 proportions results in a new polymer alloy, which in contrast to one of the parent polymers, OPS, is insoluble in toluene.

The chemical composition of these polymer alloys was further investigated by *FTi.r.* spectroscopy. *Figure 3(a)* shows the spectrum of one of these alloys. A broad small stretching vibration at 1540 cm^{-1} and a sharp small peak at 1652 cm^{-1} indicate the presence of amide groups. The strong C–N stretch due to oxazoline at 1669 cm^{-1} was no longer apparent. In addition a pronounced shoulder at 1734 cm^{-1} due to the C=O of the ester part of intermolecular linkage is present adjacent to the strong carbonyl stretching band of acid at 1705 cm^{-1}. The latter band is characteristic of the acid group originally present in CPE, though its intensity is greatly reduced after the melt mixing. Amide groups are mostly characterized by the N–H stretching vibrations around 3300 cm^{-1} but we did not see any evidence of a peak in this region. There can be two possible explanations for this. The low concentration of amido–ester linkages makes it harder to detect this particular vibration. Secondly, the O–H and C=O stretching vibrations of the unreacted carboxylic acid will shield the N–H, making it invisible. It was thought that melt conditions may not be conducive to this chemical reaction, so OPS and CPE were reacted by refluxing them in xylene solution for 5 h. When examined by *FTi.r.* the spectrum was not different from the polymer alloy prepared by melt blending.

Further confirmation of this intermolecular reaction was obtained through the study of model compounds. A long chain acid, 2.ethyl hexanoic acid and 2.ethyl oxazoline were reacted under the conditions described earlier. Samples of the reaction mixture were drawn at various time intervals and their spectra were recorded. It was found that the strong C–N absorption band of oxazoline at 1669 cm^{-1} and that of the acid at 1711 cm^{-1} disappeared at the completion of the reaction, and very strong bands at 1652 and 1540 cm^{-1} (of amide) and 1737 cm^{-1} (of ester C=O) appeared. Comparison of this spectrum with that of the polymer alloy in *Figure 3* shows that the ultimate linkages in both cases have the same chemical structure. The N–H stretch band, which could not be detected in the polymer alloy is very strong in model compounds. The probable reasons for this have already been pointed out, and here again we notice that as long as hexanoic acid was in excess in the mixture the N–H stretch could be seen only as a shoulder, but after the consumption of the acid its intensity increased enormously. It appears that the same is the case for polymer alloy, where the concentration of carboxylic groups exceeds that of the amide linkages. The time–torque relationship also shows that maximum increase in torque was observed when the ratio of oxazoline to carboxylic acid was 1:6, which means that a lot of acid remains unreacted. This leads to the conclusion that the coupling reaction results in more or less unimolecular grafting. Perhaps, due to stearic hindrance, the remaining carboxylic groups are inaccessible for the chemical reaction.

In the soxhlet extraction of OPS–CPE (60/40) alloy in toluene, very little soluble fraction was obtained. However, by replacing toluene with xylene significant portions of soluble and insoluble fractions were obtained, and on increasing extraction time to one week there was a further increase in the amount of soluble fraction. This soluble fraction was rich in carboxylic acid, but the insoluble fraction also contained carboxylic acid, as can be seen in *Figure 3(a)*. This again confirms the presence of unreacted carboxylic acid.

Differential scanning calorimetry (d.s.c.) is considered to be a useful technique for characterizing polymer blends, and blends with a single transition temperature are considered to be miscible. Thermal data on OPS–CPE alloys and their dry blends is presented in *Table 2*,

Table 2 D.s.c. data on OPS–CPE alloys and blends

Sample no.	Alloys		Dry blends	
	T_m (K)	ΔH ($\times 10^3$) (J kg^{-1})	T_m/T_g (K)	ΔH ($\times 10^3$) (J kg^{-1})
OPS	–	–	378.8	0.29
CPE	–	–	370.4	55.56
1	378.1	0.33	379.5	0.12
2	369.2	3.48	370.2	10.33
3	369.3	10.46	370.1	11.67
4	368.8	12.55	371.0	17.15
5	367.3	15.40	370.3	21.92
7	369.9	31.80	371.2	31.48
4E	364.0	2.89		
4S	365.0	9.41		
4EX	363.0	7.16		
4SX	370.2	30.79		
4EXW	360.0	8.41		
4SXW	371.4	47.28		

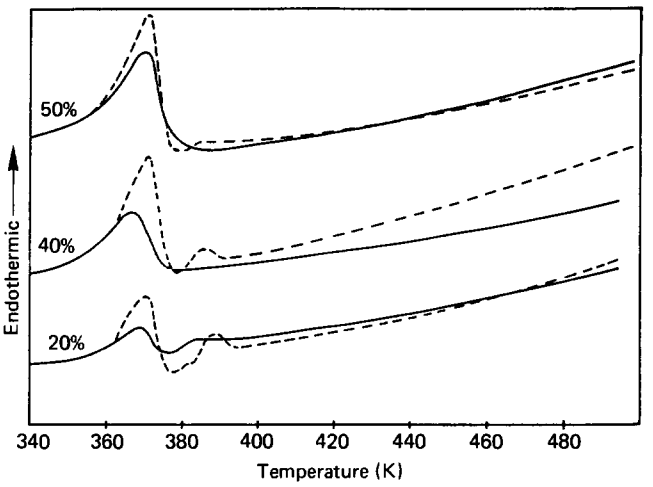

Figure 4 D.s.c. thermograms of OPS–CPE alloys (solid curves) and corresponding dry blends (dashed curves). Numbers on thermograms indicate CPE content (wt%)

and as can be seen the difference between the melting point of CPE and the glass transition temperature of OPS is only 9 K. D.s.c. thermograms of OPS–CPE alloys of different composition and their dry blends are given in *Figure 4*. Despite the small difference between T_m and T_g of the two polymers, the T_g of OPS can be vividly seen in dry blends, whereas no such distinction is observable in alloys, obtained by melt mixing. For almost every case the heat of fusion associated with the melting of CPE is less for alloys than for dry blends. Since the grafting on CPE will reduce its molecular mobility, a reduction in crystallinity is expected; but it is not total. It seems that despite grafting the CPE chain is still able to align itself, which might not have been possible if grafting had taken place all along the backbone of the polymer.

Besides the disappearance of T_g and changes in ΔH, there is no significant shift in the T_m of these blends. But more information on this was gained by obtaining thermograms of the solvent-extracted samples of 40% CPE alloy, and these are shown in *Figure 5*. Very little polymer was soluble in toluene so there is very little difference in the melting points of soluble and insoluble fractions. This suggests that the extracted portion differs primarily in molecular weight rather than composition. When the same alloy was extracted in boiling xylene for 24 h this difference becomes about 8 K, which further broadens up to 10 K after extraction for one week. As both OPS and CPE are soluble in boiling xylene the insoluble fraction with much lower T_m and ΔH than the soluble fraction must be a coupled polymer. Its *FT*i.r. spectrum in *Figure 3*, showing amido–ester linkages, also supports this assertion.

Morphological features of the fractured surfaces of the polymer blends provide sufficient information for the evaluation of their ultimate mechanical properties. Generally, it is understood that firm anchoring of the dispersed polymer phase in the matrix imparts improved physical properties. Through specific interactions, the magnitude of enthalpy of mixing of polymer pairs can be increased to a certain extent and more compatible blends can be obtained. It has been suggested that this can be achieved with varying degrees of success via covalent crosslinks, hydrogen bonding, ion–dipole interactions, dipole–dipole interactions, charge transfer complexation, and metal coordination[12]. Among these hydrogen

bonding is the most common, and takes place between halogen-containing polymers such as PVC and oxygen-containing polymers like polyesters[13]. Metal coordination type specific interactions between zinc-neutralized sulphonated EPDM and (styrene–vinylpyridine) copolymers are reported to influence the properties of the blends positively[13]. The coupling of polystyrene with EPDM rubber via Lewis acid initiated melt reaction also resulted in an improvement in the mechanical properties of these blends[14]. Despite these successes a precise correlation between the types of specific interaction, miscibility of the blends, and their ultimate physical properties is yet to be established. Since no such specific interactions are known in PS and PE blends, these blends have relatively poor physical properties; and attempts had been made to improve their properties by adding block and graft copolymers[1].

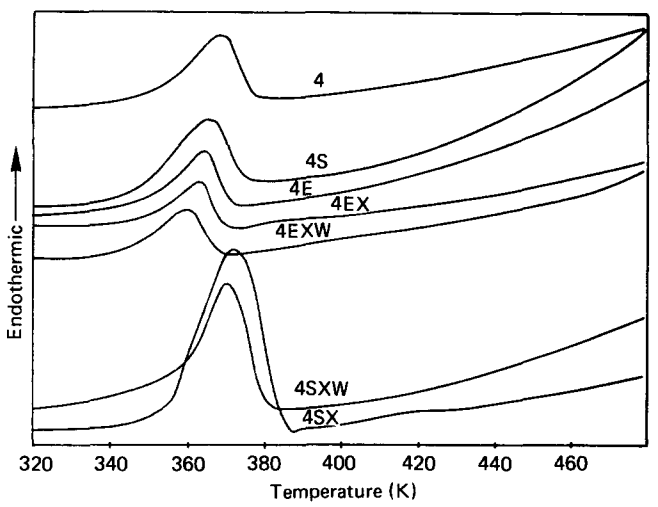

Figure 5 D.s.c. thermograms of OPS–CPE alloys before and after extraction. (4) OPS–CPE (60/40) alloy before extraction; other numbers on the curves are explained in *Table 1*

Preliminary findings on OPS–CPE blends show finer dispersion[6]. In this work the microstructure of these alloys were investigated in more detail. Some SEM micrographs of OPS–CPE alloys and of their corresponding PS–PE blends are shown in *Figure 6*. The micrographs of PS–PE blends in *Figure 6(a),(b)* reveal morphology typical of an incompatible blend. The PE dispersed domain has a well defined spherical shape. With increase in PE content from 20 to 40% the average particle size increases from 3 to 7 μm, though a few exceptionally large size particles could be observed. In each case the domain surface is very smooth, as are the cavities left behind by the PE particles during fracture. This is due to the poor adhesion. On the other hand, the micrographs of OPS–CPE alloys in *Figure 6(c),(d)* show a very different morphology. There is a fine and uniform dispersion with no precise shape and size of the domains. The very small holes, if considered to be created by the pulling out of the soft CPE component, have ruptured surfaces with no distinct shape. From the size of these 'holes' it appears that 40% CPE alloy has larger particle size (0.4 μm) than the 20% CPE alloy (0.1 μm). Some of

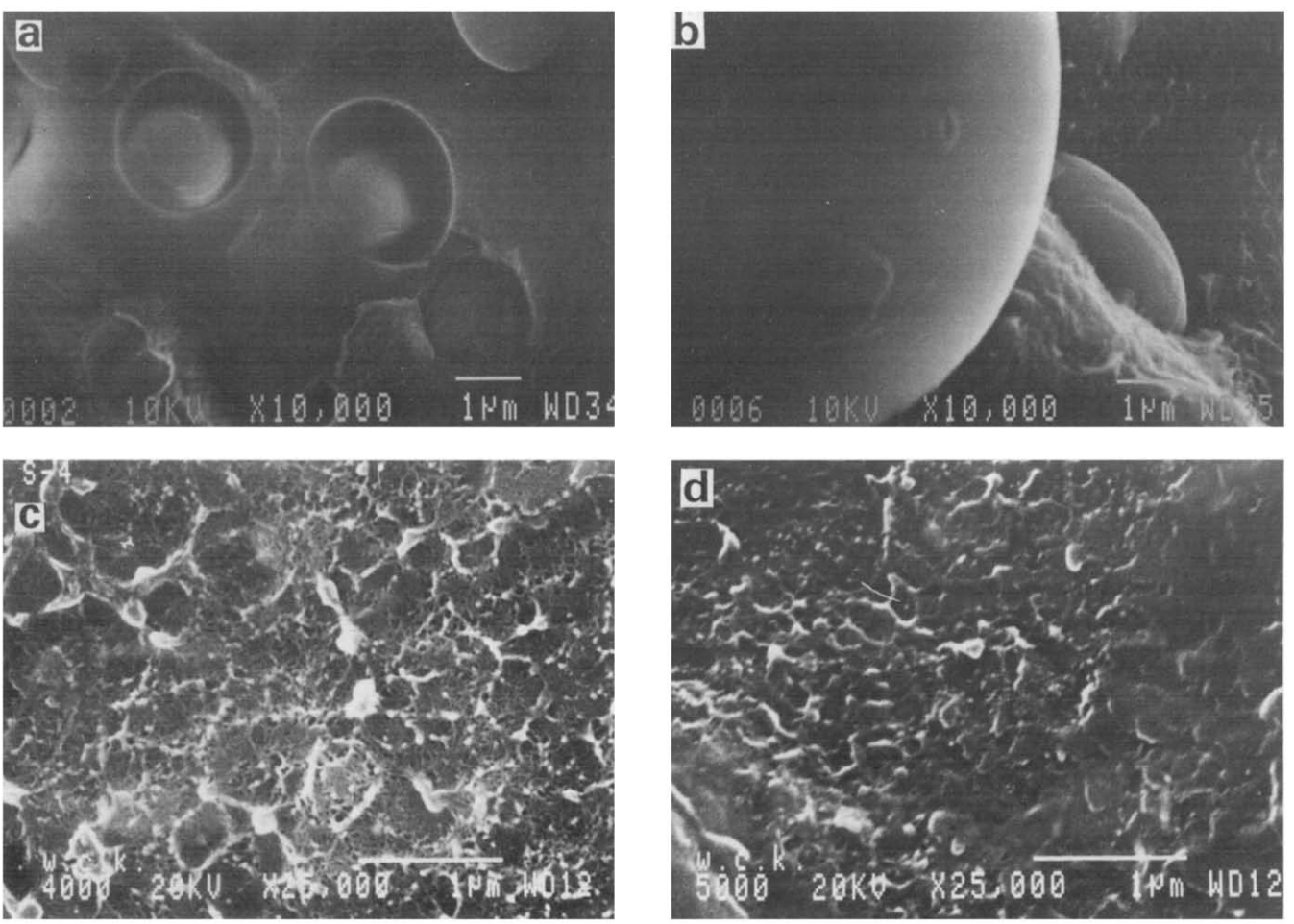

Figure 6 SEM micrographs: (a) PS–PE (80/20); (b) PS–PE (60/40); (c) OPS–CPE (80/20); (d) OPS–CPE (60/40)

these particles are completely disordered in shape and penetrate down into the matrix.

All this suggests that there is very good adhesion between the two phases, and it is the result of intermolecular reaction between the two polymers. This reinforces our torque, *FT*i.r. and d.s.c. evidence for this chemical reaction. The graft polymer formed during the melt mixing results in an alloy with good interfacial adhesion. Similar results were obtained for a poly(ethylene-methacrylic acid)/polyamide system, where grafting reaction between acid and amine end groups has been reported[12]. In that case the improved interfacial adhesion was associated with the lowering of interfacial energy.

From some preliminary tests it was found that OPS–CPE alloys have improved mechanical properties over their counterpart PS–PE blends. Further work in this direction is in progress and will be the subject of our next communication.

CONCLUSIONS

To meet the present demand of producing new polymeric materials from existing ones, it is possible to produce a polystyrene–polyethylene alloy in melt. This does not require the addition of block or graft copolymers or other compatibilizers, and it also excludes the use of peroxide for crosslinking purposes. The graft copolymer is formed by the reaction between the functional groups of OPS and CPE, during melt mixing. The graft copolymer can be separated through xylene extraction, and its d.s.c. results show that its first-order transition lies 10 K below the original polymer and also that its ΔH is much lower. Qualitative information obtained by *FT*i.r. confirms the presence of amido–ester linkages. However, more quantitative information will be necessary to understand the nature of this reaction. The OPS–CPE alloy has fine morphological features, showing strong adhesion; and hence improved mechanical properties are expected for this alloy. Also, this alloy has a potential to be used as a compatibilizer for other incompatible systems.

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